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<b>(54) Title:</b> DRILLING MUD  <b>(57) Abstract</b> <p>The present invention relates to an invert emulsion drilling mud having a continuous oil phase substantially free of mineral oil; a disperse aqueous phase; emulsifier means; weighting agent means. In one aspect of the invention the oil phase consists essentially of a natural triglyceride ester oil which oil has a substantially reduced gum content. In another aspect the oil phase consists essentially of a natural triglyceride ester oil and a non-toxic biodegradable viscosity reducing diluent, said emulsion has a pH which is not strongly alkaline and is substantially lime-free, and said emulsifier means is effective under not strongly alkaline substantially lime-free conditions.</p> <p>112 50, 51, 53-55 57, 58, 85 50, 51 53, 54, 55, 85 57, 58 ALLOW 56 14, 18, 20</p>		

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DRILLING MUD

The present invention relates to drilling muds and more particularly drilling muds suitable for use in drilling for the exploitation of oil and/or natural gas in off-shore and  
5 other environmentally sensitive situations.

It has previously been proposed to use natural animal and vegetable oils in drilling fluids. As discussed in US-A-5,232,910 though such previous proposals suffered from substantial disadvantages including high viscosity and  
10 hydrolysis of the oil component by the alkaline components e.g. lime ( $\text{Ca}(\text{OH})_2$ ) used in drilling fluids in order to, inter alia, prevent corrosion. US-A-5,232,910 seeks to avoid these problems by avoiding the inclusion of the triglyceride esters which normally constitute such  
15 animal/vegetable oils, and using instead monofunctional alcohol esters generally obtained by chemical modification of the oils comprising hydrolysis of the natural oils, separation of the acid components, and re-esterification thereof with suitable alcohols. This additional processing  
20 is however inconvenient and can result in additional expense.

It is an object of the present invention to avoid or minimize one or more of the above disadvantages.

It has now surprisingly been found that natural triglyceride  
25 ester oils with relatively high viscosity can be satisfactorily used in drilling fluids with minimal hydrolysis problems if suitable diluents are included to reduce viscosity and provided that the emulsion is substantially lime-free, and that highly alkaline conditions  
30 are avoided and/or substantially unrefined vegetable oils are avoided.

The present invention provides an invert emulsion drilling mud having a continuous oil phase substantially free of mineral oil; a disperse aqueous phase; emulsifier means;  
35 weighting agent means; characterised in that: said oil phase

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consists essentially of a natural triglyceride ester oil which oil has a substantially reduced gum content.

As discussed further hereinbelow, natural triglyceride ester oils contain considerable amounts of gums e.g. up to around 5 % v/v or more and we have found that if the gum content of such oils is substantially reduced e.g. to 2% v/v or less, then the undesirable hydrolysis of the oils can be substantially reduced or avoided.

The present invention further provides an invert emulsion drilling mud having a continuous oil phase substantially free of mineral oil; a disperse aqueous phase; emulsifier means; weighting agent means; characterised in that: said oil phase consists essentially of a natural triglyceride ester oil which has been substantially degummed and a non-toxic biodegradable viscosity reducing diluent, said emulsion has a pH which is not strongly alkaline and is substantially lime-free, and said emulsifier means is effective under not strongly alkaline substantially lime-free conditions.

The present invention also provides an invert emulsion drilling mud having a continuous oil phase substantially free of mineral oil; a disperse aqueous phase; emulsifier means; weighting agent means; and preferably fluid loss inhibition means, characterised in that: said oil phase consists essentially of a natural triglyceride ester oil and a non-toxic biodegradable viscosity reducing diluent, said emulsifier means is effective at substantially non-alkaline pH, and said emulsion has a substantially non-alkaline pH and is substantially lime-free.

We have found that hydrolysis of the vegetable oil leading to loss of performance can be substantially avoided or at least restricted to acceptable levels if the mud is made substantially lime-free and excessively alkaline or acid conditions are avoided. Drilling muds traditionally contain substantial amounts of lime and thus are more or less highly

alkaline (pH greater than 13), in order to avoid corrosion. Surprisingly we have found, though, that corrosion is not, in practice, a significant problem with drilling muds which are entirely lime-free and even mildly acidic, though as further discussed hereinbelow, hydrolysis can be contained to acceptable levels even when up to around 0.14%, w/v of lime is present corresponding to pH values of around 12.5 in the aqueous phase, provided more or less highly refined vegetable oil is used. When less refined grades of oil are used then a less-alkaline pH should be used.

In accordance with the present invention the oils used are substantially degummed i.e. more than 50% v/v of the gum content has been removed. Preferably the oils used are at least of super-degummed grade as used in chemical manufacturing. Advantageously the oils are of a substantially fully refined grade which is more or less readily available e.g. as so-called "edible-grade" oil. In general the greater the degree of refinement, the greater the reduction in susceptibility to hydrolysis that can be achieved. In practice we have found that crude unrefined vegetable oils can contain up to around 5% v/v or more of non-glyceride components or so-called gums which are multicomponent mixtures containing such things as phosphate esters, sterols, triterpene alcohols, fatty alcohols, waxes and minerals, which have the potential to act as surface-active agents and thereby influence the rapeseed oil hydrolysis process; itself an interfacial phenomenon. Thus in accordance with the present invention there is preferably used a vegetable oil containing not more than 2%, most preferably not more than 0.5%, advantageously not more than 0.25%, v/v of gums.

Suitable combinations of pH, lime content, and gum content in the vegetable oil (i.e. degree of refinement) can be readily determined by simple trial and error. In general there may be used a pH in the range from 4 to 12.5, preferably from 5 to 12, advantageously from 6 to 11.

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Thus with a drilling mud of the present invention it is possible to provide environmentally acceptable drilling muds based on readily available natural triglyceride ester oils, which muds have operating characteristics and performance  
5 comparable to those of previously known drilling muds, and which are reasonably stable under normal operating conditions.

Particularly suitable natural triglyceride ester oils that may be mentioned include vegetable oils which are  
10 triglyceride esters of long-chain (12 to 24 carbon atoms), saturated or preferably unsaturated, carboxylic acids of the type commonly described as fatty acids, which are liquid at standard temperature and pressure. Particularly suitable vegetable oils include rapeseed, olive, sunflower, peanut,  
15 palm kernel, grape seed, safflower and corn oils.

In general the relative amounts of the principal components, that is the oil phase, water phase, weighting agent etc. are comparable to those in conventional drilling muds. Thus the oil phase will generally comprise from 20 to 99, e.g. 20 to  
20 80, advantageously from 35 to 99, preferably from 50 to 99% v/v of the drilling mud and the dispersed water phase from 0 to 80%, preferably 0 to 50%, desirably from 0 to 20, most preferably from 0 to 10, e.g. 2 to 10, advantageously from 3 to 8% v/v. The weighting agent is generally used in an  
25 amount of from 0 to 40% v/v, depending upon the requirements of the drilling conditions encountered and the remaining components usually do not exceed 10, generally 3 to 5%, v/v of the drilling mud.

In order to bring the viscosity of the oil phase down to an  
30 operationally suitable level, generally not more than 30cSt, preferably not more than 15cSt, at 40°C, there is used a suitable viscosity reducing diluent. Desirably this has a relatively high flash point; preferably not less than 65°C, advantageously not less than 70°C, most preferably not less  
35 than 100°C, and a viscosity of not more than about 10cSt at 40°C. Suitable diluents include medium length hydrocarbon

chain alcohols, and ethers and esters based on medium length hydrocarbon chain alcohols. As used herein the expression "medium length" hydrocarbon chain generally indicates C5 to C15. Preferably there are used diluents wherein the "alcoholic" hydrocarbon chain length is from C6 to C10, e.g. C8. Specific diluents of this type that may be mentioned include:

Esters: 2-ethylhexyl acetate, di-2-ethylhexyl adipate, or 2-ethylhexyl oleate;

10 Ethers: dipropylene glycol monomethyl ether, di-isodecyl ether or di-octylether; and

Alcohols: Octan-2-ol

We have also found that aliphatic hydrocarbons are particularly convenient for use in the drilling muds of the invention. Hydrocarbons which have suitably high flash points and low viscosity as indicated above include linear alpha-alkenes having a hydrocarbon chain length of from C<sub>1</sub> to C<sub>22</sub>, preferably from C<sub>14</sub> to C<sub>20</sub>. Although branched chain hydrocarbons are less preferred, they may be used provided they are substantially free of short chain (generally less than C<sub>6</sub>) branches.

The diluent, and indeed the various other additives, should also, at least when in combination with the other components in the drilling mud, be non-toxic and environmentally acceptable. Non-toxicity and acceptability are conveniently evaluated by means of the so-called PARCOM Tests established by the Paris Commission which establish standards for low toxicity and low bioaccumulation, and low persistence i.e. biodegradation, as follows:

30 1. Toxicity is determined for three categories of marine organism:

\*primary producers (72 h test using the marine single-celled alga *Skeletonema costatum*)

\*herbivore (48 h test using the marine crustacean copepod

35 *Acartia tonsa*)

\*sediment dweller (10 day test using the marine amphipod

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*Corophium volutator*)

The first two tests estimate the hazard of the drilling mud in the water column, while the third, as the name suggests, estimates the hazard of the material in the sediment (which is the primary environmental fate compartment for discharged solid waste). Few current drilling muds exhibit significant water column toxicity, and consequently evaluation often rests on the results of sediment toxicity tests. The first two tests estimate short-term (acute) toxicity and require the drilling mud to be non-toxic at drilling mud concentrations up to 1000 mg/l of water.

For products which are of acceptably low acute toxicity, there may nevertheless still be a residual concern about the potential of the base fluid for bioaccumulation and long-term toxic effects.

2. Bioaccumulation concerns are addressed by the estimation of the octanol-water partition coefficient, generally using the OECD 117 guideline for HPLC determination. In cases where it is believed that this measurement may overestimate bioaccumulation potential, a direct measurement of bioaccumulation may be carried out using the marine mussel *Mytilus edulis*.

3. Biodegradability and the potential persistence of drilling mud components (in particular, the base fluid in invert emulsion systems) are addressed by measurements of aerobic and anaerobic degradation. These tests are conducted in accordance with a number of OECD and ISO guidelines, and at present require a minimum of 60% degradation within the test period (28-56 days) in order to be considered 'readily' degradable.

Evidence of ready aerobic degradability (i.e. amenability to oxidative metabolism) can be used in conjunction with the results of *Mytilus* bioaccumulation tests (in particular, the rate of base fluid depuration from tissue) to provide a good



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indication of the extent to which a base fluid is likely to be significantly accumulated through the food chain.

The amount of diluent used may be varied within relatively wide limits depending on inter alia the desired drilling mud viscosity and the viscosity of the individual natural oil(s) used therein. In general there may be used from 5 to 60%, preferably from 10 to 50%, advantageously from 25 to 40 e.g. about 25%, v/v of diluent in the oil phase.

In addition to the reduction of the high viscosity due to the vegetable oil component, we have also found that the diluent used can additionally lead to a significant reduction in hydrolysis of the triglyceride ester. This affords a useful degree of flexibility in relation to other parameters of the drilling muds of the invention, for example, to allow the inclusion of small lime concentrations up to say 0.14% w/v, and/or reduction of the degree of refinement of the vegetable oil e.g. allowing the use of vegetable oils containing up to 3% v/v of gums.

In general the various additives used should be compatible with and/or capable of functioning effectively under substantially non-alkaline conditions.

Various suitable substantially non-alkaline capable emulsifier means are known in the art including oleophilic fatty acid salts such as those based on amido amines of the general formula  $NZ$ , wherein  $Z$  represents  $RCONH(CH_2)_n$  - where  $R$  is a long chain hydrocarbon, generally  $C_8$  to  $C_{24}$  and other amido amines of the general formula  $NHZX$  wherein  $Z$  has the same meaning as before and  $X$  is, for example, ethoxylate. Generally these are used with a suitable carrier or solvent such as a glycol ether. A typical commercially available product is Interdrill Emul HT (Trade Mark) from the Schlumberger Dowell Company of London, England. Other suitable emulsifiers that may be mentioned include alkylbenzene sulphonates and imidazolines.

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Suitable weighting agents known in the art are heavy metal minerals such as those based on barium e.g. barite, or iron e.g. haematite. In general these are used in an amount sufficient to increase the specific gravity of the mud to 5 from 1.0 to 2.5 g/cm<sup>3</sup>, and are generally used in an amount of from 5 to 30% v/v in the mud.

Various "activity" control means are known in the art for preventing loss of the aqueous phase into the rock strata through which drilling is taking place, and include alkali 10 or alkaline earth metal salts such as CaCl<sub>2</sub>, NaCl, and KCl.

Provided they are not otherwise specifically excluded from the drilling muds of the present invention, any other additive conventionally used in drilling muds may be included in the drilling muds of the present invention. 15 Thus for example there may be used a viscosity control or thickening agent such as an organophilic clay e.g. an organically treated smectite clay such as that available under the Trade Name: "Interdrill Vistone" from Schlumberger Dowell of London, England, or finely divided bentonite. 20 Also there may be used an oil wetting agent to improve the oil wettability of the inorganic weighting material and other solid material present in the drilling fluid. Suitable agents include one or more of an alkyl benzene sulphonate and a fatty imidazoline salt. A suitable 25 commercially available product is Interdrill OW (Trade Name) available from Schlumberger Dowell Ltd. of London, England.

Further preferred features and advantages of the present invention will appear from the following examples given by way of illustration.

30 Examples 1 to 3 - Preparation of Drilling Muds

Invert drilling muds were prepared using a natural (i.e. not chemically modified) triglyceride ester rapeseed oil which had the following composition: 61% mono-unsaturated (predominantly oleic); 31% polyunsaturated (predominantly 35 linoleic) and 8% saturated fatty acids. The oil used had

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been partially refined and was of super-degummed grade with a gum content of approximately 2% v/v.

The oil was mixed with the emulsifier: Emul HT; the oil-wetting agent: Interdrill O/W; and the organophilic clay: Vistone. Calcium chloride was dissolved in water and the resulting brine added to the stirred oil mixture. The resulting emulsion was stirred for approximately five minutes before barite was added, and the complete mixture was then stirred for a further 30 minutes. The maximum temperature of the mixture was controlled by the use of a water bath and was limited to 60-70°.

Three different muds were prepared with different proportions of the above components as set forth in Table 1 hereinbelow.

15 Table 1

Component	Quantity (g/lab barrel)		
	Formulation 1	Formulation 2	Formulation 3
Rapeseed Oil	250.0	187.0	167.2
Oil-wetting Agent	1.0	1.0	1.0
Emulsifier	3.0	3.0	3.0
20 Organophilic Clay	7.8	7.8	7.8
Water	25.7	25.7	26.3
Calcium Chloride	10.0	10.0	12.2
Diluent	nil	55.5	50.8
Barite	120.3	120.3	256.7
25 Specific Gravity	1.2	1.2	1.5

#### Examples 4 to 6 - Performance of Drilling Muds

The performance capabilities of the drilling muds of Examples 1 to 3 were assessed as follows: The prepared muds were hot rolled at 120°C for sixteen hours and characterised using the API (American Petroleum Institute) Recommended Practice for the evaluation of oil-based drilling muds: 13B-2. This

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relates to a practical situation in which drilling mud may remain in situ in a drill hole for up to 15 hours during a drill bit change.

Further samples of the formulations were subjected to a  
5 prolonged hot rolling period of seventy two hours and recharacterised to demonstrate the substantial stability and resistance to hydrolysis of the drilling muds of the invention. The results are summarised in Table 2 hereinbelow.

10 Table 2

Rheological Property	FORMULATION 1			FORMULATION 2			FORMULATION 3		
	Fresh	Hot Rolled 16 hours	Hot Rolled 72 hours	Fresh	Hot Rolled 16 hours	Hot Rolled 72 hours	Fresh	Hot Rolled 16 hours	Hot Rolled 72 hours
Apparent viscosity (cP)	80	78.5	58.5	45	47.5	42	66.5	59	66
15 Plastic Viscosity (cP)	71	67	51	38	41	35	52	46	53
Yield Points (lb/100ft <sup>2</sup> )	18	23	15	14	13	14	29	26	26
10 sec gel	10	10	6	7	8	6	13	14	12
20 10 min gel	12	11	7	9	9	7	15	16	14
Electrical Stability (volts)	1574	1610	>2000	1964	1666	>2000	>2000	>2000	>2000

As may be seen from the above Table, the electrical  
stability remained well above 1000 volts throughout  
25 indicating good stability of the emulsion and resistance to de-emulsification of the oil-water emulsion. The gel strength (resistance to settling out of weighting agent and drill cuttings) was also substantially preserved even after the extended hot rolling test.

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Example 7 - Effects of Diluents on Partly Degummed (2% gum) Rapeseed Oil

Table 3

	Diluent	Concentration (lb/barrel)	Percentage Triglyceride Hydrolysis After Hot Rolling (120 °C, 72 Hours)
5	Diluent-free	0	50.8%
	Octan-2-ol	57.1	40.0%
	Dipropylene glycol Monomethyl ether	66.2	42.6%
	Di-iso-decyl ether	57.8	50.9%
10	2-Ethylhexyl acetate	60.3	38.5%
	Di-2-ethylhexyl Adipate	64.7	40.8%

\* Equivalent to 25% v/v of rapeseed oil present in the drilling mud formulation.

15 Example 8 - Effect of Gum Content on Rapeseed Oil Hydrolysis

The effect of added gum on the hydrolysis of a drilling mud based on edible grade rapeseed oil (containing less than 0.2 % gum) with the composition shown in table 4 is shown

20 in Table 5 from which it may be seen that hydrolysis increases dramatically with increasing gum content.

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TABLE 4

Component	Concentration (lb/barrel)
Edible Grade Rapeseed Oil	187.0
2-Ethylhexyl Acetate	55.5
5 Emul HT	3.0
Vistone	7.8
Water	25.7
CaCl <sub>2</sub>	12.2
Barite	120.3

10 TABLE 5

Gum Content (lb/barrel)	Percent Triglyceride Hydrolysis After Hot-Rolling (120 °C, 72 Hours)
0	6.7%
5	14.9%
15 10	28.5%

Example 9 - Use of Hydrocarbon Diluent in Drilling Mud

The effect of using of different amounts of hydrocarbon diluent commercially available under the Trade Name Ultidrill on triglyceride hydrolysis of an edible grade rapeseed oil based drilling mud, is shown in Tables 6 and 7. In the case of samples 2 and 3, an alternative organophilic clay Truvis (also available from Schlumberger-Dowell), which is effective at lower concentrations, was used in place of Vistone. A conventional fluid loss additive, Truflo MVO (available from Schlumberger-Dowell), was also included to inhibit loss of drilling fluid into the drilled formation.

TABLE 6

Component	Quantity (lb/barrel)		
	Sample 1	Sample 2	Sample 3
Edible Rapeseed Oil	187.1	132.5	130.2
Ultidril	53.4	62.1	61.1
5 Interdrill OW	1.0	1.0	1.0
Emul HT	3.0	6.0	6.0
Vistone	7.0	nil	nil
Truvis	nil	2.0	4.0
Truflo MVO	2.0	3.0	3.0
10 Water	26.0	25.29	25.17
CaCl <sub>2</sub>	12.2	7.35	7.31
Barite	127.5	348.0	350.4

Table 7

Sample 1

Sample 2

Sample 3

Rheological Properties	BHR	*AHR	BHR	*AHR	BHR	*AHR
15 Apparent Viscosity (cP)	43.5	39.5	75	85	63	66
Plastic Viscosity (cP)	36	35	61	69	54	53
Yield Point (lb/100 ft <sup>2</sup> )	15	9	28	32	18	26
Fann 6 rpm reading	8	6	16	18	15	14
10 second gel	9	5	16	16	15	12.5
20 10 minute gel	12	6	20	18	20	15
Electrical stability (volts)	1453	1609	>2000	1353	>2000	1651
Triglyceride Hydrolysis (%)	nil	6.8	nil	10.4	nil	10.3

BHR - Before Hot-Rolling    AHR - After Hot-Rolling    \* - Hot-rolling at 120 °C, 72 hrs.

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Example 10 - Lime Tolerance of Substantially Degummed  
Rapeseed Oil Drilling Mud

The tolerance of edible grade Rapeseed Oil based Drilling mud with the composition shown in Table 8, to increasing  
5 amounts of added lime, is shown in Table 9 from which it can be seen that triglyceride hydrolysis is limited to acceptable levels at added lime levels of up to around 0.4 lb/barrel after hot-rolling for 72 hours at 120°C. A  
conventional fluid loss additive Truflo 100 (similar to  
10 Truflo MVO in Example 9) was also included in the drilling mud.

Table 8

	Component	Quantity (lb/barrel)
	Edible Grade Rapeseed Oil	130.3
15	Ultidrill	61.0
	Emul HT	6.0
	Interdrill FL	1.0
	Truflo 100	3.5
	Truvis	4.0
20	CaCl <sub>2</sub>	7.31
	Water	25.71
	Barite	350.4



Rheological Property	Quantity of Lime Added to Each Sample (lb/barrel)													
	0		0.1		0.2		0.3		0.4		0.5		1.0	
	BHR	AHR	BHR	AHR	BHR	AHR	BHR	AHR	BHR	AHR	BHR	AHR	BHR	AHR
Apparent Viscosity (cP)	69.5	77	65	75	69.5	71	70	68.5	71.5	70	68.5	76	72	69
Plastic Viscosity (cP)	56	61	57	60	56	55	56	54	58	54	56	60	57	57
Yield Point (lb/100 ft <sup>2</sup> )	27	32	24	30	27	32	28	29	27	32	23	32	30	24
Fann 6 rpm Reading	17	18	14	16	16	17.5	16	16	16	16	15	17	17	12
10 second gel	17	17	14	15	16	16	16	15	15.5	14	15	16	18	10
10 minute gel	20	20	18	18	20	19	21	18	19	18	18	19	21	120
Electrical Stability (volts)	2000	1534	2000	1621	2000	1791	2000	1738	2000	1796	2000	1801	2000	1261
Triglyceride Hydrolysis %	nil	10.4	nil	12.8	nil	10.2	nil	9.7	nil	16.9	nil	28.0	nil	72.0

[illegible]

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CLAIMS

1. An invert emulsion drilling mud having a continuous oil phase substantially free of mineral oil; a disperse aqueous phase; emulsifier means; weighting agent means;  
5 characterised in that: said oil phase consists essentially of a natural triglyceride ester oil which oil has a substantially reduced gum content.
2. An invert emulsion drilling mud having a continuous oil phase substantially free of mineral oil; a disperse aqueous  
10 phase; emulsifier means; weighting agent means;  
characterised in that: said oil phase consists essentially of a natural triglyceride ester oil and a non-toxic biodegradable viscosity reducing diluent, said emulsion has  
15 a pH which is not strongly alkaline and is substantially lime-free, and said emulsifier means is effective under not strongly alkaline substantially lime-free conditions.
3. A mud according to claim 2 wherein said oil is at least partly degummed.
4. A mud according to claim 1 or claim 3 wherein said oil  
20 has a gum content of not more than 2% v/v.
5. A mud according to claim 4 wherein said oil has a gum content of not more than 0.5% v/v.
6. A mud according to claim 4 wherein said oil is of an edible-grade.
- 25 7. A mud according to any one of claims 1 to 6 which contains not more than 0.14% v/v of lime.
8. A mud according to any one of claims 1 to 7 which has a pH value of not higher than 12.5.
9. A mud according to claim 8 which has a pH value in the  
30 range from 4 to 11.

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10. A mud according to any one of claims 1 to 9 wherein said diluent has a flash point not lower than 65°C.

11. A mud according to any one of claims 1 to 10 wherein said diluent has a viscosity of not more than 10cSt at 40°C.

12. A mud according to any one of claims 1 to 11 wherein said diluent is selected from aliphatic hydrocarbons, aliphatic hydrocarbon alcohols, and ethers and esters of aliphatic hydrocarbon alcohols.

13. A mud according to claim 12 wherein the diluent comprises a saturated or unsaturated hydrocarbon having a hydrocarbon chain length of from C<sub>10</sub> to C<sub>22</sub>.

14. A mud according to any one of claims 1 to 13 which contains from 5 to 60% w/w of diluent in the oil phase.

15. A mud according to claim 14 which contains from 25 to 40% w/w of diluent in the oil phase.

16. An invert emulsion drilling mud having a continuous oil phase substantially free of mineral oil; a disperse aqueous phase; emulsifier means; weighting agent means; and preferably fluid loss inhibition means, characterised in that: said oil phase consists essentially of a natural triglyceride ester oil and a non-toxic biodegradable viscosity reducing diluent, said emulsifier means is effective at substantially non-alkaline pH, and said emulsion has a substantially non-alkaline pH and is substantially lime-free.

# INTERNATIONAL SEARCH REPORT

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PCT/GB 95/00680

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C09K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP-A-0 374 671 (HENKEL) 27 June 1990  see page 3, line 7 - line 44 see page 3, line 57 - page 5, line 5 see page 5, line 12 - line 37 see page 6, line 16 - line 54 ---	1,2,8,9, 12,16
Y,P	EP,A,0 625 563 (CALGENE CHEMICAL INC.) 23 November 1994 see page 2, line 8 - line 31 see page 3, line 24 - line 30 see page 3, line 48 - line 57 ---  -/--	1,2,12, 16

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

23 June 1995

Date of mailing of the international search report

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# INTERNATIONAL SEARCH REPORT

Internat. Application No  
PCT/GB 95/00680

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>EP-A-0 374 672 (HENKEL) 27 June 1990</p> <p>see page 3, line 7 - line 29</p> <p>see page 4, line 38 - line 48</p> <p>see page 5, line 13 - line 57</p> <p>see page 6, line 58 - page 7, line 12</p>	1,2,8,9, 12,16
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Y	<p>US,A,4 631 136 (R.W.JONES) 23 December 1986</p> <p>see column 3, line 32 - column 4, line 35</p> <p>see column 5, line 52 - column 6, line 3</p>	1

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